# I. POLAROGRAPHIC INVESTIGATIONS OF TUNGSTEN COMPLEXES

# II. MULTIPURPOSE INSTRUMENT FOR ELECTRICAL MEASUREMENTS

BY

WILLIAM ARTHUR ZIEGLER

A.B., University of Illinois, 1948
M.S., University of Illinois, 1949

## AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS
1952

# I. POLAROGRAPHIC INVESTIGATIONS OF TUNGSTEN COMPLEXES

# II. MULTIPURPOSE INSTRUMENT FOR ELECTRICAL MEASUREMENTS

BY

WILLIAM ARTHUR ZIEGLER

A.B., University of Illinois, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1952

URBANA, ILLINOIS
1952

## ACKNOWLEDGMENT

The author wishes to express his gratitude to Dr. H. A. Laitinen for his suggestion of this interesting problem and his inspiring direction of the research.

The author also wishes to thank Mr. Arthur E. Wood and Mr. Verle F. Walters for their part in the construction and maintenance of the multipurpose instrument for electrical measurements and to thank Mr. Walters in particular for his much valuable advice concerning its construction and operation.

And to his wife Margaret the author is most grateful for her untiring assistance in preparing the thesis and for her constant encouragement.

R. UNIV.
BIBLIOTHEEK
LEIDEN

# I. POLARGRAPHIC INVESTIGATIONS OF TUNGSTEN COMPLEXES

## Historical and Introduction

One of the most striking features of tungsten chemistry is the insolubility of tungsten ions in acid solution. However, a slight solubility in concentrated halogen acids was attributed in 1910[9] to complex formation, and this theory has been well substantiated by subsequent work. Usually in concentrated hydrochloric acid medium, tungsten(VI) has been reduced chemically to tungsten(V) by liquid bismuth amalgam and to tungsten(III) by liquid lead, cadmium, and zinc amalgams.[11] Reduction with tin has been reported to yield tungsten in oxidation states +3, +4, and+5.[1,7,8,10] These three lower oxidation states have also been obtained by electrolytic reductions employing various cathodes.[2,3]

Lingane and Small[6] reported that a polarographic investigation showed that tungsten(VI) in various concentrations of hydrochloric acid was reduced to tungsten(V), which in turn was reduced to tungsten(III) in a reversible two-electron process. Three forms of tungsten(III) were discussed: an anodically inert green form of the composition $W_2Cl_9^{-3}$, a yellow form, and a red form, which is transformed to the yellow species on further electrolysis or heating. Both anodic polarograms and controlled potential oxidations indicated that the two latter forms were oxidized to tungsten(IV) rather than passing directly to tungsten(V).

Although the oxidation states of tungsten could be readily determined, little was known of the complexes involved. With a view toward furthering the knowledge of these complexes, this study was undertaken.

## Experimental and Discussion

Preliminary experiments showed that all quantitative

work with lower oxidation states of tungsten must be done in the absence of air. Contrary to a report in the literature,[11] only red tungsten(III) instead of the yellow form could be obtained with liquid lead amalgam. No form of tungsten(VI) could be extracted from hydrochloric acid with organic solvents, excluding ether, which is known to form complexes with tungsten.

Tungsten(VI) was reduced to tungsten(V) at a mercury cathode by controlled potential electrolysis. Polarograms were obtained of both tungsten(V) and tungsten(VI) in various concentrations of hydrochloric acid. In no case did the logarithmic plots of the waves obtained for the reduction of tungsten(V) to tungsten(III) obey the criteria of reversibility; the points did not consistently fall on single straight lines, and slopes were far too high for a two-electron reduction. In 12 *M* acid the logarithmic plots yielded two straight lines of different slopes which intersected at the half-wave potential, as if to suggest the possibility of formation of an intermediate tungsten(IV) complex during the reduction. Therefore, it was concluded that the reduction of tungsten(V) to tungsten(III) is not a reversible two-electron process.

An attempt was made to learn the compositions of the tungsten complexes involved by studying the shifts of half-wave potential with varying hydrogen ion and chloride ion concentrations. The study failed because of the irreversibility of the process and the lack of a suitable acid to use for maintaining constant hydrogen ion concentration as chloride concentration was decreased.

In the series of experiments in which the concentration of hydrogen ion was kept constant by using greater quantities of perchloric acid as the hydrochloric acid concentration was decreased, abnormally high currents for the reduction wave of tungsten(VI) were observed. These currents increased with perchloric acid concentration. A dip at the end of the tungsten(V) wave appeared in the medium consisting of 5 *M* hydrochloric and 7 *M* perchloric acids. This dip grew with

increasing perchloric acid concentration so that in 0.04 *M* hydrochloric and 12 *M* perchloric acids the entire tungsten(V) wave had disappeared, and the current of the tungsten(VI) wave was 100 times the normal value that would be obtained in concentrated hydrochloric acid only.

The extraordinarily high current was shown to be roughly proportional to the concentration of tungsten(VI) and subject to kinetic rather than diffusion control. In a microelectrolysis using the dropping mercury electrode, 15.39 times the number of coulombs required for the reduction of all tungsten(VI) to tungsten(V) were passed with only a 27.9% reduction in the current. This experiment proved the existence of an extraneous reaction undoubtedly catalyzed by tungsten(V).

Polarograms of tungsten(VI) in a medium of 0.04 *M* hydrochloric and various perchloric acid concentrations showed that with less than 6 *M* perchloric acid the tungsten could not be kept in solution. The current decreased, though not proportionately, with decreasing perchloric acid concentration. In solutions containing 11.5 *M* perchloric acid and various hydrochloric acid concentrations, it was found that in the range of chloride concentrations from 0.015 to 0.34 *M* a catalytically less active complex of tungsten(V) was formed with increasing chloride concentration.

It was shown chemically that tungsten(V) reduces perchloric acid. Experiments indicated the reduction product to be chloride, although this was not proved.

## II. MULTIPURPOSE INSTRUMENT FOR ELECTRICAL MEASUREMENTS

Lingane[4,5] has descrribed an instrument for performing several electrochemical operations. A similar instrument, largely patterned after his designs, was constructed in this laboratory although there were numerous improvements and

modifications. It can be used for the following purposes:

1. Automatically recording potentiometric titration curves.
2. Performing titrations which automatically stop at a preset end-point.
3. Conducting manual potentiometric titrations.
4. Performing automatically controlled potential electrolyses.
5. Performing electrolyses at constant current.

The heart of this instrument is a Brown Potentiometer, which is used both as a recording indicator and as a controller for the automatic operations. The construction and manner of operation of the various components are described, and detailed instructions are given for the use of the instrument.

## BIBLIOGRAPHY


1. Chernikhov, Y. A., and Goryushima, V. G., *Zavodskaya Lab.* **11**, 137-41 (1945); *C. A.* **40**, 1110 (1946)
2. Collenberg, O., and Backer, J., *Z. Elektrochem.* **30**, 230-8 (1924)
3. *Gmelins Handbuch der anorganischen Chemie*, Berlin, Verlag Chemie, 1933, 8th Ed., No. 54
4. Lingane, James J., *Anal. Chem.* **20**, 285-92 (1948)
5. Lingane, James J., *Anal. Chem.* **21**, 497-9 (1949)
6. Lingane, James J., and Small, Lyndon A., *J Am. Chem. Soc.* **71**, 973-8 (1949)
7. Olsson, O., *Ber.* **46**, 566-82 (1913)
8. Olsson, O., *Z. anorg. Chem.* **88**, 49-73 (1914)
9. Rosenheim, Arthur, and Bernhardi-Grisson, R., *7th International Congress of Applied Chemistry* **10**, 120-7 (1910)

10. Rosenheim, Arthur, and Dehn, Eitel, *Ber.* 48, 1167-78 (1915)

11. Someya, Kinichi, *Z. anorg. u. allgem. Chem.* **145**, 168-80 ( 1925)

# VITA

William Arthur Ziegler was born on February 10, 1924, in St. Louis, Missouri. He attended elementary school in Carmi, Illinois, and graduated from the Carmi Township High School in 1941. In the autumn of that year he entered DePauw University, where he completed three semesters before entering the Army in January, 1943. While in the service, he attended Brown University for one year as a student in the Army Air Force Pre-Meteorology "C" Course. Later he attended the Officers' Radar School at the Massachusetts Institute of Technology for three months. After discharge from the Army Air Force in 1946, he entered the University of Illinois. In the summer of 1947 he was employed as a chemist in the control laboratory of the Grasselli Chemicals Department of E. I. du Pont de Nemours and Company in East Chicago, Indiana. In February, 1948, he graduated with the degree of Bachelor of Arts and immediately entered the Graduate College of the University of Ilinois. He received the degree of Master of Science in June, 1949. On October 13, 1951, he was married to Miss Margaret Anne Robbins of Urbana, Illinois.

During his four years in graduate school he held a Teaching Assistantship in the Analytical Division of the Chemistry Department. He is a member of Alpha Chi Sigma, Phi Lambda Upsilon, Sigma Xi, the American Chemical Society, and the American Association for the Advancement of Science.